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DOE STANDARD

Destructive Assay Methods Compendium

U.S. Department of Energy
Washington, D.C. 20585

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FOREWORD

1. This Department of Energy standard is approved for use by all DOE Components and their contractors.

2. Beneficial comments (recommendations, additions, and deletions) and any pertinent data that may improve this document should be sent to the U.S. Department of Energy, New Brunswick Laboratory, Attention: Ms. Kimberly Johnson–Miller, 9800 South Cass Ave, Bldg. 350, Argonne IL 60439 by letter or to the e-mail address Kimberly.Johnson-Miller@CH.DOE.GOV . Please include if possible the Document Improvement Proposal form (DOE F 1300.3) appearing at the end of this document.

3. DOE technical standards, such as this standard, do not establish requirements. However, all or part of the provisions in a DOE standard can become requirements under the following circumstances:

    (1) They are explicitly stated to be requirements in a DOE requirements document; or

    (2) The organization makes a commitment to meet a standard in a contract or in an implementation plan or program plan required by a DOE requirements document.

Throughout this standard, the word "shall" is used to denote actions which must be performed if the objectives of this standard are to be met. If the provisions in this standard are made requirements through one of the two ways discussed above, then the "shall" statements would become requirements. It is not appropriate to consider that "should" statements would automatically be converted to "shall" statements as this action would violate the consensus process used to approve this standard.

The Preparing Agency would like to acknowledge the following authors of the document: Price Russ at the Lawrence Livermore National Laboratory; Robert Marshall at the Los Alamos National Laboratory; Doyle Hembree at the BWX Y-12 Plant ; Michael Holland at the Savannah River Site and Wanda Mitchell at the New Brunswick Laboratory.

Destructive Assay Methods Compendium[1]

I. Scope

Analytical chemistry plays a key role in nuclear material control and accounting (MC&A). A large part of Special Nuclear Material (SNM) inventories and virtually all of the highly attractive SNM inventories are based on sampling bulk materials followed by destructive assay (DA) of these materials. These measurements support MC&A in process control, physical inventory verification, evaluation of the effects of process changes, detecting and resolving shipper-receiver differences, and the resolution of IAEA inspector-facility differences. The evaluation and the specification of DA, MC&A techniques have proven difficult, in part, because of the highly specialized and technical nature of DA and because of the wide variety of methods and applications. This compendium is provided as a resource for those selecting methods for use and for those evaluating the performance of MC&A measurements.

II. Purpose

The purpose of this guidance document is to:

- Recommend criteria to use in evaluation of DA MC&A capabilities.
- Provide a basis for selection of appropriate upgrades where capabilities are inadequate to support MC&A goals.
- Provide a list of DA methods suitable for MC&A with the following information:
  - ➢ performance and applications information,
  - ➢ strengths and limitations,
  - ➢ references and information on cost.

III. Applicability

DA involves measurements on samples taken from a larger quantity or batch; typically samples are altered by their preparation such that the sample is not returned to the batch.   This document is limited to analytical methods used to quantify and characterize plutonium (Pu) and enriched uranium (EU). The US DOE and NRC identify these materials as Special Nuclear Materials (SNM).

- Limited guidance is provided on bulk measurements and sampling of bulk materials.
- All the included methods, alone or in conjunction with other methods, provide analysis of SNM element or isotope quantities and are appropriate for use in support of MC&A. Most of these methods may also provide information useful for process control.
- Some methods listed herein address the determination of impurities present in SNM. These methods are limited to those typically used to measure impurities to provide interference corrections for certain DA methods.
- Appendix A provides summary information on DA methods. General references are listed which provide in-depth information on each method. For reviews of SNM assay (elemental concentration) methods References 1-4 are recommended.

IV. DA Method Evaluation and Selection Criteria.

The primary criterion for evaluating a DA method used in support of MC&A is determining whether or not the method provides the accuracy required to support statements on inventory assurance. Material Control and Accounting goal quantities are defined to determine the appropriate combination of MC&A elements, including DA and non-destructive assay (NDA) measurements, which support statements of allowable inventory difference. The US approach to inventory assurance encourages and supports using highly precise and accurate analytical measurement

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values in inventory difference calculations. As processing of SNM has been shut down, more limited US funds have been made available for DA MC&A measurements and a more practical approach may be needed to determine the best use of the available resources. Within established Material Balance Areas (MBAs), MC&A goal-quantities for those MBA's can then be used to evaluate existing analytical capabilities and to determine the upgrades required. Nuclear Regulatory Commission (NRC) and International Atomic Energy Agency (IAEA) target values and goal quantities are provided for guidance in Appendix B.

With goal quantities defined, the SNM flow in a specified time period can be estimated, the fraction of that flow which would be determined by analytical chemistry can be estimated, and the acceptable percent uncertainty on the flow for the analytical measurements can be estimated. These estimates allow the precision and accuracy of the analytical measurements required to attain the declared level of assurance to be determined. Note that the performance requirements for DA depend upon the attractiveness of the material. It is absolutely essential that the overall error, which includes the combined errors from every stage of the measurement process, be considered in determining the required precision and accuracy of the analytical method. In general, the precision of the DA method must be higher than that required to simply meet a given level of assurance because errors from other sources, particularly sampling, must be taken into account. A good rule of thumb is that the DA method should contribute no more than 20% to the overall allowable error. Appendix C presents an example of the type of calculation needed to evaluate the limits on DA errors consistent with detecting a goal-quantity loss of SNM from a hypothetical MBA.

A second criterion is technological suitability. All DA methods require some level of technological support, but the requirements vary widely. Readily available electronic and computer support may be needed for some methods together with high purity chemicals and certified reference materials (CRMs). Without these support resources, certain DA methods may be unusable. Each site must include an estimate of the availability of these resources to evaluate the feasibility of sustaining selected methods at a particular facility.

A third criterion is cost effectiveness. DA methods vary widely in their costs to set up and operate. Sustainability bears consideration as additional US facilities are removed from operation.

A fourth criterion is the capacity or throughput of each method. Some methods are relatively labor intensive and can only provide a few analyses per day; others are highly automated and can provide many analyses per day. Automation may be desirable not only to increase the sample throughput, but also to reduce variability in the data.

A fifth criterion is training. In general where chemists are employed, they are knowledgeable and skilled in the methods they employ. However, implementing new or enhanced DA methods at facilities may require training of chemists, technicians and support personnel which adds to the cost of implementing the methods.

V. Sampling and bulk measurements.

The DA of samples alone does not provide a statement of the uncertainty on the SNM inventory for MC&A. The DA of a sample provides the elemental or isotopic information which is multiplied by the mass or volume of the bulk material from which the sample is taken. The calculated SNM mass in the bulk material has an uncertainty which includes uncertainties in the bulk material measurement (mass or volume), the degree to which the sample represents the bulk material, and the quality of the DA measurement.

The capability of the facility to take samples representative of the bulk material must be understood by the DOE oversight and the facility so that sampling error can be included in the calculation of the overall SNM inventory uncertainty. Failure to collect representative samples from bulk SNM can mask theft or cause false alarms, which undermines the credibility of MC&A systems. Therefore, tasking the facility to evaluate its sampling error contribution to inventory difference is advised to

identify inadequacies in sampling practices and to establish the accuracy and precision associated with sampling.

Overall analytical uncertainty depends on both sampling and DA errors. When assessing DA measurement requirements versus assurance goals, the chemist must have a reasonable knowledge of the type and magnitude of the errors from the sample collection process. Since the error from sampling and the DA result on the sample are multiplied by the bulk mass or volume, which is typically a large number, to yield the bulk SNM quantity, the accuracy and precision needed in the measurement of the bulk mass or volume must be carefully considered. The chemist must also know the ability of the laboratory to detect larger than expected sampling errors (by other than the replicate DA measurements). If the laboratory can readily validate a set of replicate samples by a bulk measurement such as sample density measurements (and process tank density measurements, if available), then sample error can be quantified, or at least bounded. Under optimum conditions, sample validation can control and minimize otherwise undetected sampling error, thus DA method selection can be based more strictly on measurement uncertainty requirements. If sample validation methodology is not implemented the reliability requirements for DA measurements must be increased to ensure detection of sample errors from limited data sets on replicate DA measurements. Enhancement of a facility's capabilities for sampling bulk SNM, understanding sampling errors, and measuring bulk volumes or masses to the sufficient level of precision and accuracy may need to be made in parallel with enhancement of DA methods.

Destructive Assay Methods Compendium

Appendix A.

In this appendix, a list of the more common SNM assay and isotopic ratio methods and some supporting impurity measurement methods are provided. For each method a very concise description of the method, sample size and preparation, support equipment and supplies, calibration and standards, performance, and advantages and disadvantages are given. References are given for comprehensive information on the more complicated methods. Where references are not given use References 3 and 4 on the preceding page.

Cost estimates are based upon implementation of a capability, and include the costs for equipment, instrumentation, training and supplies. Exact costs will be facility specific. To provide rough guidance, the Team has broken the cost into the following categories: LOW = <100K dollars; MEDIUM = 100 to 500K; HIGH = >500K

METHOD A.1.1: Ignition/Gravimetry of Pu	
ELEMENT DETERMINED	Pu
BASIC PRINCIPLE	Convert a weighed portion of plutonium sample to PuO_2, a compound of known, specific composition, by heating (ignition) in a furnace to 1200 $^\circ$C or higher, and calculate the quantity of plutonium from the known composition and the total final mass of the PuO_2 formed. Correct the final weight of PuO_2 for any nonvolatile impurities as determined by separate analysis
TYPICAL RESULTS	Random and Systematic errors of 0.05% to 0.2%.
SAMPLE SIZE	5 - 10 grams
SAMPLE TYPES	High purity plutonium materials
ADVANTAGES	Laboratory equipment required is simple. High precision for high purity materials is readily attained. Operator time per determination is small. Solid samples require minimal handling.
LIMITATIONS	Requires known, reproducible composition of the final weighing form, PuO_2. Application is limited to high purity materials such as plutonium oxalate, plutonium oxide, plutonium metal, and plutonium nitrate solutions. Nonvolatile impurities must be separately determined and a correction applied. Weighing errors.
REFERENCES	K. A. Swinburn and I. R. McGowan, "An Approach to the Use of Plutonium Dioxide as a Chemical Reference Standard for Plutonium," BNFL-205(W), British Nuclear Fuels Limited, 1975. G. R. Waterbury, R. M. Douglas, and C. F. Metz, "Thermogravimetric Behavior of Plutonium Metal, Nitrate, Sulfate and Oxalate," *Anal. Chem.*, 33,1018-1023 (1961).
COST ESTIMATE	LOW

METHOD A.1.2: Controlled Potential Coulometry of Pu	
ELEMENT DETERMINED	Pu
BASIC PRINCIPLE	Quantitative electrolytic oxidation of Pu(III) to Pu(IV) at an electrode maintained at a controlled potential with determination of the quantity of Pu from the quantity of electricity required for the complete oxidation. (Special case of redox titrimetry in which electrons are used as the titrant.)
TYPICAL RESULTS	Random and systematic errors of 0.1% readily attained. For better sample types errors of 0.05% are attained.
SAMPLE SIZE	1 - 10 mg Pu
SAMPLE TYPES	Pu metal, oxides Mixed U, Pu oxides Pu nitrate solutions Dissolver solutions Applicable to most Pu materials when ion-exchange separation is used.
ADVANTAGES	High precision and accuracy on relatively small quantities of Pu. Relatively free of interferences. Readily automated. Adaptable to remote operations and analysis of irradiated materials.
LIMITATIONS	Moderately complex/moderately expensive instrumentation. Electrolysis cell and electrode malfunctions. Several interferences cause problems. Weighing errors. Operator errors.
REFERENCES	W. D. Shults, "Applications of Controlled-Potential Coulometry to the Determination of Plutonium-A Review," *Talanta*, Vol. 10, 1963, p. 833-849. T. L. Frazzini, M. K. Holland, J. R. Weiss, and C. E. Pietri, "A Digital Integrator for Controlled-Potential Coulometry," *Analytica Chimica Acta*, Vol. 129, 1981, p. 125. ASTM Standard Test Methods for Controlled-Potential Coulometric Measurement of Pu, C 1108 and C 1165, both in Volume 12.01 International Standard, "Controlled-Potential Coulometric Assay of Plutonium," ISO 12183.
COST ESTIMATE	MEDIUM

METHOD A.1.3: Alpha Spectrometry of Pu	
ELEMENT DETERMINED	Pu (^{238}Pu in support of mass spectrometry)
TYPICAL RESULTS	Random error of 2% for 0.01% ^{238}Pu.
BASIC PRINCIPLE	From an alpha spectrum of a dissolved and separated Pu sample, determine a ratio from measurements of the total counts from the ^{238}Pu peak regions and ^{239}Pu + ^{240}Pu peak regions. Calculate the ^{238}Pu abundance from the ratio obtained and abundance measurements of ^{239}Pu and ^{240}Pu obtained from mass spectrometry of a separate portion of the sample.
SAMPLE SIZE	Samples containing 0.01 - 0.7 weight percent ^{238}Pu
SAMPLE TYPES	Used where the ^{238}Pu abundance is too low for mass spectrometric measurement or there is interference from ^{238}U. Pu must be dissolved and separated.
ADVANTAGES	Allows determination of ^{238}Pu where problems occur with mass spectrometry. Method is relatively simple and fast.
LIMITATIONS	Separation from ^{241}Am is required. Mass spectrometric determination of ^{239}Pu and ^{240}Pu is required. Preparation of counting disk to obtain uniform sample distribution requires care. Uncertainties in Pu isotope half-lives.
REFERENCES	
COST ESTIMATE	LOW

METHOD A.1.4: Alpha Counting of Pu	
ELEMENT DETERMINED	Pu
TYPICAL RESULTS	Random and systematic errors of 2 - 5%
BASIC PRINCIPLE	A sample or a separated Pu fraction is mounted on a counting disk and the gross alpha activity is determined.
SAMPLE SIZE	Adequate to give 1 - 5 X 10^5 counts in 5 - 10 minutes
SAMPLE TYPES	Dissolver solutions, irradiated process solutions and waste solutions.
ADVANTAGES	Method is relatively simple and fast. Applicable to radioactive solutions requiring remote handling.
LIMITATIONS	Specific activity of the Pu in the sample must be known. Generally requires a separation. Thick or nonuniform deposits on counting disks cause errors. None quantitative Pu recovery from separations cause errors.
REFERENCES	
COST ESTIMATE	LOW

METHOD A.1.5: Ceric Titration of Pu	
ELEMENT DETERMINED	Pu
TYPICAL RESULTS	Random and Systematic errors are 0.05% on good materials.
BASIC PRINCIPLE	Oxidimetric titration of Pu(III) to Pu(IV) using the oxidant Ce(IV) as titrant with spectrophotometric detection of the end point which is observed as a color change of the added ferroin indicator or potentiometric endpoint; the Pu in the initial sample is reduced prior to the titration using a lead reductor column.
SAMPLE SIZE	200 to 250 mg Pu
SAMPLE TYPES	Pu metal, Pu oxides, Pu nitrides Used primarily for relatively pure metal due to interferences. (Use anion exchange separation when several interferences are present)
ADVANTAGES	Simple laboratory equipment. High precision and accuracy on applicable samples.
LIMITATIONS	Subject to numerous common interferences - Fe, Cr, Ti, Mo, W, U, V Relatively large sample size required. Titrant – tedious and lengthy preparation; requires standardization and careful storage; uncertainty of standards used yield errors. Operator errors - weighing errors, titration errors.
REFERENCES	J. Corpel and F. Regnaud, *Analytica Chimica Acta.*, Vol. 27, pp. 36-39, 1962.
COST ESTIMATE	LOW

METHOD A.1.6: Amperometric Titration of Pu	
ELEMENT DETERMINED	Pu
TYPICAL RESULTS	Random errors of 0.1 -0.2% are generally attained. Systematic errors are usually better than 0.1%. Random errors under the best conditions are better than 0.05%.
BASIC PRINCIPLE	Reductimetric titration of Pu(VI) to Pu(IV) using the reductant Fe(II) as titrant with amperometric detection of the end point after preliminary oxidation of the Pu to Pu(VI) using excess Ag(II) oxide as an oxidant. Amperometric titration is based on observation of the change in current at a working electrode as titrant is added. In this titration the electrode responds to the Fe(II) titrant; when the end point is exceeded a current flow proportional to the excess Fe(II) is observed allowing detection and determination of the end point.
SAMPLE SIZE	10 - 60 mg Pu
SAMPLE TYPES	Pu as metal, oxide, fluoride, chloride, nitrate, sulfate. Pu in alloys containing uranium, iron, cobalt and aluminum.
ADVANTAGES	Simple laboratory equipment. High precision and accuracy on relatively small samples. Clear, simple end point detection. Initial oxidation state of Pu does not matter; all Pu is oxidized to Pu(VI).
LIMITATIONS	Subject to several interferences - cerium, chromium, vanadium and manganese. Titrant – requires daily standardization; subject to change. Initial titration reaction is slow and difficult to follow. Indicator and reference electrodes subject to problems.
REFERENCES	C. A. Seils, Jr., R. J. Meyer, and R. P. Larsen, "Amperometric Titration of Plutonium (VI) with Iron (II)," *Anal. Chem. 35*, pp. 1673-1675, 1963.
COST ESTIMATE	LOW

METHOD A.1.7: Spectrophotometry of Pu (and U)	
ELEMENT DETERMINED	Pu (and U)
TYPICAL RESULTS	Routine samples, Random errors of 1 - 3%; systematic errors of 0.5% High purity plutonium materials, Random error of 0.3%; systematic error of 0.2%
BASIC PRINCIPLE	Rapid determination of the concentration of specific oxidation states of U and Pu by simultaneous measurement of the absorption of light by those oxidation states over a range of wavelengths and fast computer processing of the data based on calibration models.
SAMPLE SIZE	0.2 - 200 g/L U or Pu
SAMPLE TYPES	U and Pu solutions with U(VI) and Pu(III) or Pu(VI)
ADVANTAGES	Rapid measurements. Reasonable precision. Easily interfaced to processes; reliable online measurements. Rugged instrument - no moving parts.
LIMITATIONS	Spectral and chemical interferences. Absorption is temperature and matrix dependent. Calibration model errors (weighing and absorption measurement errors). Operator errors - sample preparation.
REFERENCES	D. R. Van Hare, "Analysis of Special Recovery Samples by Pu (III) Spectrophotometry," Savannah River Plant Report DP-1713, 1985. "Interference Study of the Pu(III) Spectrophotometric Assay," *Journal of Radioanalytical and Nuclear Chemistry,* Vol 152, No. 1, 1991, pp. 207-218.
COST ESTIMATE	LOW

METHOD A.2.1: Ignition/Gravimetry of U	
ELEMENT DETERMINED	U
BASIC PRINCIPLE	Convert a weighed portion of uranium sample to U_3O_8, a compound of known, specific composition, by heating (ignition) in a furnace open to the air and calculate the quantity of uranium from the known composition and the total final mass of the U_3O_8 formed. Nonvolatile impurities must be determined by a separate determination.
TYPICAL RESULTS	Random errors of 0.01 to 0.08% and Systematic errors of 0.01 to 0.02%.
SAMPLE SIZE	5 - 10 grams
SAMPLE TYPES	High purity uranium materials - metal, UO_2, UO_3, U_3O_8, UF_4, UF_6, Uranyl nitrate solution
ADVANTAGES	Laboratory equipment required is simple. High precision is readily attained. Operator time per determination is small. Solid samples require minimal handling.
LIMITATIONS	Requires known, reproducible composition of the final weighing form, U_3O_8. Application is limited to high purity materials; impurity content and corrections can be problems. Weighing errors.
REFERENCES	O. A. Vita, C. R. Walker, and E. Litteral, "The gravimetric Determination of Uranium in Uranyl Nitrate," *Anal. Chimica Acta.*, Vol 64, pp. 249-257, 1973. F. B. Stephens, R. G. Gutmacher, K. Ernst, J. E. Harrar, and S. P. Turel, "Methods for the Accountability of Uranium Dioxide," NUREG-75/010, pp. 4-44 to 4051, U.S. Regulatory Commission , June 1975.
COST ESTIMATE	LOW

METHOD A.2.2: Davies/Gray Titration of U	
ELEMENT DETERMINED	U
BASIC PRINCIPLE	Redox titration of U(IV) to U(VI) with potentiometric end point detection after chemical pretreatment of the sample solution to adjust the oxidation states of species present so that uranium is essentially the only substance titratable by the oxidant.
TYPICAL RESULTS	Random and systematic errors of 0.1% readily attained. For better sample types errors of 0.05% are attained.
SAMPLE SIZE	10 - 50 mg U
SAMPLE TYPES	Applicable to uranium materials from essentially all stages of the nuclear fuel cycle - uranium ores, metal, oxides, salts and alloys.
ADVANTAGES	Good precision and accuracy are readily attained. Laboratory equipment is relatively simple. Few interferences; most can be removed or controlled. Groups of 12 - 15 samples handled together. Relatively easily automated.
LIMITATIONS	Operator errors; requires strict adherence to details. Requires full time and attention of analyst. Requires care in selection and testing reagents. Indicator and reference electrode problems occur. Errors/changes in titrant value. Weighing errors.
REFERENCES	W. Davis and W. Gray, "Rapid and Specific Volumetric Method for the Precise Determination of Uranium Using Ferrous Sulfate as Reductant," *Talanta*, 1964, p. 1203. A.W. Eberle and M. W. Lerner, "Effect of Added Vanadyl Ion on the Accuracy of the New Brunswick Laboratory Method (Ferrous Ion Reduction) of Determining Uranium," NBL-258, 1971, p. 22.
COST ESTIMATES	LOW for Manual MEDIUM if Automated

METHOD A.2.3: Laser-Induced Kinetic Phosphorescence	
ELEMENT DETERMINED	U
BASIC PRINCIPLE	The method utilizes the measurement of the intensity of the green phosphorescence of U which results from excitation with ultraviolet light from a pulsed nitrogen/dye laser. The phosphorescence of the UO_2^{+2} is filtered, amplified, and measured by a computer which also calculates the result. To prevent quenching of the phosphorescence, a phosphate-based complexing reagent is added. The kinetic analysis of the uranyl phosphorescence provides a highly precise and accurate measurement, thus, eliminating the need for an internal standard.
TYPICAL RESULTS	Precision of 3% for solutions with 0.001 - 5.0 μg U/g solution. Accuracy of 2% for 0.001 – 5.0 μ U/g solution
SAMPLE SIZE	0.001 – 5.0 μg U/g solution Detection limit is 2 X 10^{-5} μg
SAMPLE TYPES	Low and trace level U solutions.
ADVANTAGES	Method is rapid and relatively simple. Sensitive to low levels of U. Generally directly applicable to solutions without separations. Pu does not interfere.
LIMITATIONS	Uranium must be present as U(VI). Contamination with U from reagents or sample treatments must be carefully avoided. Alcohols, halides, and oxidizable metals are strong quenching agents which interfere with phosphorescence of uranium. Other materials such as chromate may absorb at the same excitation wavelength as uranium (425 nm). Suspended particles interfere with the normal decay curve of uranium phosphorescence.
REFERENCES	W. Campen and K. Bachmann, "Laser-Induced Fluorescence for the Direct Determination of Small Concentrations of Uranium in Water, " <u>Mikrochim. Acta</u> [Wien], 1979 II, pp. 159-170. A. C. Zook, L. H. Collins, and C. E. Pietri, "Determination of Nanogram Quantities of Uranium by Pulsed-Laser Fluorimetry," <u>Mikrochim. Acta</u> [Wien], 1981 II, pp. 457-468.
COST ESTIMATE	LOW

Method A.2.4 Spectrophotometry of U (See Method A.1.7)

Method A.2.5: Densitometry	
Physical Property Measured	Density in mass per volume. Very precise specific gravity values may be calculated at specified temperatures from the measured density at specified temperatures.
BASIC PRINCIPLE	A vibrating hollow U-shaped tube is caused to oscillate at a high frequency. The frequency squared of the tube oscillation is proportional to the mass of the tube. Filling the hollow tube with a liquid changes the mass of the tube and the tube oscillation. The density meter is calibrated by injection of two standards of different density into the hollow tube and measuring the tube oscillation for each standard. The density of an unknown sample is determined by relating the tube oscillation of the sample to the tube oscillation of the standards. Temperature is controlled either with a constant temperature bath or Peltier cooler.
TYPICAL RESULTS	Instrumentation is available that provides density values to four, five, or six decimal places.
SAMPLE SIZE	Approximately 1 ml.
SAMPLE TYPES	Any liquid that can be injected with a syringe and not vigorously attack glass. Instruments are available that have stainless steel U tubes instead of glass.
ADVANTAGES	Very fast analyses, easy to automate, data obtained in electronic format and easy to transmit electronically. Very precise temperature control (instrumentation easy to calibrate at various temperatures). Instruments operate for years with minimal maintenance.
LIMITATIONS	Suspended solids and air/gas bubbles can interfere.
REFERENCES	Calculating Density Meter with a built-in thermostat, DMA 46 Instruction Manual, Anton Paar™, Graz/AUSTRIA.
COST ESTIMATE	LOW

METHOD A.3.1: Mass Spectrometry: Isotopic Abundance of U and Pu	
ELEMENT DETERMINED	U & Pu
TYPICAL RESULTS	Random and systematic errors of 0.01 - 0.1% depending on sample size.
BASIC PRINCIPLE	Conversion of a sample to a gaseous, ionic form; separation of the ions according to their mass to charge ratios in a magnetic field; and measurement of the relative intensities of the separated ion beams.
SAMPLE SIZE	U - 10^{-8} to 10^{-5} g Pu - 10^{-9} to 10^{-6} g
SAMPLE TYPES	All U & Pu materials - after separation
ADVANTAGES	Method gives essentially complete isotopic information over a wide range of isotopes with good precision and accuracy. Requires very little sample. Instrumentation is readily automated.
LIMITATIONS	Complex, expensive instrument requires care in operation; mass discrimination and nonlinearities require corrections. Usually require separations due to problems from interferences and impurities.
REFERENCES	"Thermal Ionization Mass Spectrometry of Uranium with Electrodeposition as a Loading Technique", D.J. Rokop, et al., Anal. Chem., 54 957 (1982). "High-precision Isotopic Analyses of Uranium and Plutonium by Total Sample Volatilization and Signal Integration", E.L. Callis and R.M. Abernathey, Int. J. Mass Spect. Ion Processes, 103 93-105 (1991).
COST ESTIMATE	HIGH

METHOD A.3.2: Isotope Dilution Mass Spectrometry of U and Pu	
ELEMENT DETERMINED	U & Pu
BASIC PRINCIPLE	Variation of mass spectrometry involving addition of a known quantity of enriched isotope (Spike) to the sample which allows calculation of the elemental concentration from the measured isotopic ratios of the mixture, the measured ratios of an unspiked sample, and the known isotopic composition of the spike.
TYPICAL RESULTS	Random and systematic errors of 0.25%
SAMPLE SIZE	U - 10^{-8} to 10^{-5} g Pu - 10^{-9} to 10^{-6} g
SAMPLE TYPES	All U & Pu materials - subject to availability of Spike materials
ADVANTAGES	Method determines both isotopic composition and elemental concentration. Good precision and accuracy can be achieved. Requires only small amounts of sample.
LIMITATIONS	Complex, expensive instrumentation. Problems with attaining chemical and isotopic equilibration. Inadequate separation of U and Pu. Uncertainties in assay of spike solutions. Weighing errors for the sample or spike. Mass spectrometer operational errors.
REFERENCES	"The Determination of Plutonium by Mass Spectrometry Using a 242-Plutonium Tracer," R. K. Webster, A. A. Smales, D. F. Dance, and L. J. Slee, Anal. Chim. Acta 24 371-380 (1961). "The Application of Isotope Dilution Mass Spectrometry to the Determination of Uranium and Plutonium in Nuclear Fuels," J. E. Rein and C. F. Metz, in Analytical chemistry of Nuclear Fuels, Proc. Panel, Vienna, July 13-17, 1970, (International Atomic Energy Agency, Vienna, Austria, 1972), pp. 97-109. The Use of a Combined Internal Standard and Assay Spike for the Isotope Dilution Mass Spectrometric Assay of Plutonium, D. W. Crawford, M. A. Legel, M. I. Spaletto, and N. M. Trahey, NBL-318(a), pp. 17-19, March 1988. "Isotope Dilution Mass Spectrometry," K.G. Heumann, in Inorganic Mass Spectrometry, edited by F. Adams, R. Gijbels, and R. Van Grieken. John Wiley and Sons, New York, 1988, pp. 301-376.
COST ESTIMATE	LOW (assumes suitable mass spectrometer already available, a HIGH cost item)

METHOD A.4.1: Spectrophotometry for iron	
ELEMENT DETERMINED	Fe
BASIC PRINCIPLE	Iron is measured spectrophotometrically as the Fe(II) o-phenanthrolate complex at a wavelength of 508 nm after removal of plutonium by oxalate precipitation. The quantitiy of iron is calculated from the measured absorbance and the absorbance per microgram of iron obtained for prepared solutions having known iron contents. [Fe Standard prepared from electrolytic iron or ferrous ammonium sulfate hexahydrate.]
TYPICAL RESULTS	The relative standard deviation is approximately 1%.
SAMPLE SIZE	10-40 micrograms Fe [capability to 1 microgram with wider precision].
SAMPLE TYPES	Iron in the range 100 – 1000 μg Fe per gram of uranium-plutonium oxide
ADVANTAGES	Rapid and simple measurement to allow for iron correction of plutonium results. Typical elapsed time for analysis of 3 hours.
LIMITATIONS	If nickel is present in quantities greater than that of iron, it will produce a bias in the iron measurement that is greater than 1.5%.
REFERENCES	Los Alamos National Laboratory Report, LA-4622, "Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials," J. E. Rein, G. M. Matlack, G. R. Waterbury, R. T. Phelps, and C. F. Metz, pp 55-58, (1971).
COST ESTIMATE	LOW

METHOD A.4.2: DC Arc Emission Spectroscopy for metallic impurities	
ELEMENT DETERMINED	Metal impurities
BASIC PRINCIPLE	Powdered samples are loaded into graphite electrodes. A dc arc is induced across the electrodes producing arc temperatures from 4000 to 8000°K. Emission lines from primarily neutral atoms are detected using either photographic plates or photomultiplier tubes. Intensities of emission lines are related to those of standards to obtain quantitative information.
TYPICAL RESULTS	The technique is used to measure metal impurities in the range of 0.1 – 2000 µg/g (lower and upper limits are element specific).
SAMPLE SIZE	Electrodes are loaded with approximately 50-mg of sample. Samples are usually homogenized before loading electrodes.
SAMPLE TYPES	All types of samples (must be solid to load into electrode)
ADVANTAGES	- Relatively low cost - Large number of metal impurities detected simultaneously - Almost any sample matrix can be analyzed
LIMITATIONS	- Relatively large error (better than spark source mass spectrometry but worse than inductively coupled plasma optical emission) - Susceptible to contamination (like any impurity analysis). - Requires highly trained technician.
REFERENCES	H. H. Willard, L.L. Merritt, Jr., and J.A. Dean, *Instrumental Methods of Analysis*, 5th Ed., D. Van Nostrand, New York, 1974, p. 390.
COST ESTIMATE	Medium

METHOD A.4.3: Atomic absorption (AA), inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma emission mass spectrometry (ICP-MS)	
ELEMENT DETERMINED	Metallic sample components and isotopic composition when using ICP-MS
BASIC PRINCIPLE	Detection mechanisms: - AA: absorption of element-specific wavelengths - ICP-OES: emission of element-specific wavelengths generated by the inductively coupled plasma - ICP-MS: ions generated in an inductively coupled plasma are mass analyzed by one of several methods (e.g., quadrapole or magnetic sector mass spectrometer).
TYPICAL RESULTS	Typically, impurities can be determined from 1 – 5000 ppm.
SAMPLE SIZE	Depends on dilution factor (0.1-g or larger).
SAMPLE TYPES	Liquids and solids (solids require dissolution).
ADVANTAGES	High precision Wide dynamic range Multiple element, simultaneous analyses (with the exception of AA)
LIMITATIONS	Samples must be in solution Requires highly skilled technicians Subject to contamination
REFERENCES	
COST ESTIMATE	MEDIUM (except for AA which is LOW)

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Appendix B. International Regulations and Guidelines.

Appendix B.1. Code of Federal Regulations (CFR)

10 CFR Part 70.51

The limits of error on the material unaccounted for (MUF) on any total plant in-process MBA are:

1) Pu or ^{233}U in chemical reprocessing plant: 1.0%

2) U elemental and fissile isotope in reprocessing plant: 0.7%

3) Pu, ^{233}U, high-enriched U elemental and

    fissile isotope in all other: 0.5%

4) Low-enriched uranium element and

    fissile isotope in all other: 0.5%.

10 CFR Part 74.13

A report to the Nuclear Regulatory Commission (NRC) is required if inventory difference exceeds both:

1) Twice the standard error of the estimated measurement uncertainty associated with the inventory difference; and

2) Two hundred grams of plutonium or ^{233}U, 300 grams of high enriched ^{235}U contained in high-enriched uranium, or 9000 grams of ^{235}U contained in low enriched uranium.

Appendix B.2. International Atomic Energy Agency (IAEA) Guidance

IAEA/SG/INF/4; "IAEA Safeguards Aims, Limitations, Achievements" IAEA, Vienna, 1983, p. 26

For direct-use material, the significant quantities (SQs) have been set to coincide in weight (though not exactly in composition) with threshold amounts:

1) 8 kg of plutonium element (containing less than 80% ^{238}Pu)

2) 25 kg of ^{235}U contained in uranium enriched to 20% or more

3) 8 kg of ^{233}U

Appendix B.3. Target Values (US Department of Energy Guidance)

Target Values for Tank Volume Measurements of Solutions using a Ruska Electromanometer

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
U Solutions/Pure Pu		0.3	0.3

Appendix B.4. Target Values (Working Group on Techniques and Standards for Destructive Analysis (WGDA) of the European Safeguards Research and Development Association (ESARDA).[2])

B.4.1 Target Values for Titrimetry Measurements for Process, Product, Scrap, and Waste Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
UF_6	U[a]	0.1[3]	0.1[3]
U Solutions/pure	U	0.15	0.15
U Solutions/scrap	U[b]	0.3	0.5
U Oxide/powder, NG	U[c]	0.1[3]	0.1[3]
U Oxide/powder, scrap	U	0.3	0.5
U Oxide/sintered materials	U	0.15	0.1
UF_4 Powder/NG	U[c]	0.15	0.3
U-metal/NG	U	0.2[3]	0.2[3]
U-Al based materials/NG	U	0.2	0.3
U-Al based/scrap	U	0.3	0.5
U-Si based materials/NG	U	0.2	0.3
Zr-U materials	U	0.5	0.3
U/Carbides	U	0.3	0.5
$(Th,U)O_2$/Kernals & BISO[d]	U Th	0.15 0.2	0.2 0.2
$(Th,U)O_2$ or UO_2/TRISO[d]	U Th	0.2 0.2	0.2 0.3
U-scrap/dirty & diluted	U	0.5	2.0

[a] Control of decomposition required if subjected to chemical decomposition.
[b] Shall be free of turbidity.
[c] Control of oxidation and/or moisture pickup required.
[d] BISO, TRISO: binary, trinary sealed oxide coated particles.

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[2] P. De Bièvre, J. Dalton, S. Baumann, R. E. Perrin, T. Görgenyi, C. Pietri, E. Kuhn, and S. Deron, "1987 Target Values for the Uncertainty Components in Fissile Isotope and Element Assay," *Journal of Nuclear Materials Management*, pp. 99-106, July 1987.
[3] H. Aigner et al., " International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Material", *International Atomic Energy Agency Report,* STR-327, Millennium Edition, April 2001.

B.4.1 (continued) Target Values for Titrimetry Measurements for Process, Product, Scrap, and Waste Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
Spent Fuel inputs/	U	0.3	0.3
HWR & LWR	Pu	___	___
Spent Fuel Inputs/FBR	U	0.3	0.2
	Pu	0.3	0.2
Pu Nitrate/Pure	Pu	0.15^3	0.15^3
U,Pu Nitrate Solutions/Pure	U[a]	0.1^3	0.1^3
	Pu	0.15^3	0.15^3
PuO_2/Powders	Pu[b]	0.15^3	0.15^3
$(U,Pu)O_2$ MOX/LWR	U	0.3	0.2
	Pu[b,c]	0.5	0.5
$(U,Pu)O_2$ MOX/FBR	U	0.3	0.2
	Pu[a,b]	0.2	0.2
$(U,Pu)O_2$ MOX/Scrap	U	0.5	0.5
	Pu	1.0	0.5

---

[a] U/Pu = 3.
[b] Control of oxidation and/or moisture pickup required.
[c] 1-4% Pu.

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3   H. Aigner et al., " International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Material", *International Atomic Energy Agency Report,* STR-327, Millennium Edition, April 2001.

B.4.2 Target Values for Coulometry Measurements for Process, Product, and Scrap Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
UF$_6$	U[a]	0.2	0.2
U Solutions/pure	U	0.15	0.15
U Oxide/powder, NG	U[b]	0.15	0.15
U Oxide/powder, scrap	U	0.3	0.5
U Oxide/sintered materials	U	0.15	0.15
UF$_4$ Powder/NG	U[b]	0.15	0.3
U-metal/NG	U	0.15	0.1
U-Al based materials/NG	U	0.2	0.3
U-Al based/scrap	U	0.3	0.5
U/Carbides	U	0.3	0.5
Pu Nitrate/Pure	Pu	0.2	0.2
U,Pu Nitrate Solutions/Pure	U[c]	0.2	0.2
	Pu	0.2	0.2
PuO$_2$/Powders	Pu[b]	0.2	0.2
(U,Pu)O$_2$ MOX/LWR	U	0.3	0.2
	Pu[b,d]	0.5	0.5
(U,Pu)O$_2$ MOX/FBR	U	0.3	0.2
	Pu[b,c]	0.2	0.2
(U,Pu)O$_2$ MOX/Scrap	U	0.5	0.5
	Pu	1.0	0.5

---

[a] Control of decomposition required if subjected to chemical decomposition.
[b] Control of oxidation and/or moisture pickup required.
[c] U/Pu = 3.
[d] 1-4% Pu.

B.4.3 Target Values for Gravimetry Measurements for Process and Product Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
UF$_6$	U[a]	0.05[3]	0.05[3]
U Solutions/pure	U	0.1	0.15
U Oxide/powder, NG	U[b]	0.05[3]	0.05[3]
U Oxide/sintered materials	U	0.05	0.1
UF$_4$ Powder/NG	U[b]	0.15	0.15
U/Carbides	U	0.2	0.5
Pu Nitrate/Pure	Pu	0.1	0.15
PuO$_2$/Powders	Pu[b]	0.05[3]	0.05[3]
(U,Pu)O$_2$ MOX/LWR	U[c] Pu	0.1 ---	0.15 ---

---

[a] Control of decomposition required if subjected to chemical decomposition.
[b] Control of oxidation and/or moisture pickup required.
[c] After Pu and Am correction.

B.4.4 Target Values for K-edge Densitometry Measurements for Process, Scrap, and Waste Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
U Solutions/pure	U	0.2	0.15[3]
U Solutions/scrap	U[a]	0.2	0.2
Pu Nitrate/Pure	Pu	0.2	0.15[3]
U,Pu Nitrate Solutions/Pure	U[b] Pu	0.2 0.3	0.2 0.3
U,Pu Solutions/Waste	U Pu	0.3 ---	0.3 ---

---

[a] Shall be free of turbidity.
[b] U/Pu = 3.

[3] H. Aigner et al., " International Target Values 2000 for Measurement Uncertainties in Safeguarding Nuclear Material", *International Atomic Energy Agency Report,* STR-327, Millennium Edition, April 2001.

B.4.5 Target Values for X-ray Fluorescence Measurements for Process, Product, Scrap, and Waste Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
U Solutions/pure	U	0.5	0.5
U Solutions/scrap	U[a]	2.0	2.0
U Oxide/powder, scrap	U	1.0	1.0
Zr-U materials	U	1.0	1.0
$(Th,U)O_2$/kernals & BISO[b]	U	1.0	0.5
	Th	1.0	0.5
$(Th,U)O_2$ or UO_2/TRISO[b]	U	1.0	1.0
	Th	1.0	1.0
U-scrap/dirty & diluted	U	3.0	5.0
Spent Fuel inputs/ HWR & LWR	U	0.5	0.5
	Pu	1.0	1.0_
Spent Fuel Inputs/FBR	U	0.5	0.5
	Pu	1.0	1.0
Liquid Waste/HAW	Pu	5.0	10.0
Pu Nitrate/Pure	Pu	0.5	0.5
U,Pu Nitrate Solutions/Pure	U[c]	0.5	0.5
	Pu	0.5	0.5
U,Pu Solutions/Waste	U	3.0	5.0
	Pu	3.0	5.0
$(U,Pu)O_2$ MOX/FBR	U	0.5	0.5
	Pu[c,d]	0.5	0.5
$(U,Pu)O_2$ MOX/Scrap	U	3.0	5.0
	Pu	3.0	5.0

---

[a] Shall be free of turbidity.
[b] BISO, TRISO: binary, trinary sealed oxide coated particles.
[c] U/Pu = 3.
[d] Control of oxidation and/or moisture pickup required.

B.4.6 Target Values for Spectrophotometric Measurements for Process, Product, Scrap, and Waste Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
U Solutions/scrap	U[a]	3.0	5.0
U-scrap/dirty & diluted	U	5.0	10
Spent Fuel inputs/ HWR & LWR	U Pu	--- 1.0	--- 1.0
Spent Fuel Inputs/FBR	U Pu	--- 1.0	--- 1.0
Pu Nitrate/Pure	Pu	0.5	0.5
U,Pu Nitrate Solutions/Pure	U Pu	--- 0.5	--- 0.5
U,Pu Solutions/Waste	U Pu	5.0 2.0	5.0 2.0
PuO$_2$/Powders	Pu[b]	0.5	0.5
(U,Pu)O$_2$ MOX/LWR	U Pu[b,c]	--- 0.5	--- 0.5
(U,Pu)O$_2$ MOX/FBR	U Pu[b,d]	--- 0.5	--- 0.5
(U,Pu)O$_2$ MOX/Scrap	U Pu	--- 1.0	--- 1.0

[a] Shall be free of turbidity.
[b] Control of oxidation and/or moisture pickup required.
[c] 1-4% Pu.
[d] U/Pu = 3.

B.4.7 Target Values for Fluorimetry Measurements for Scrap Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
U Solutions/scrap	U[a]	10	10
U Scrap/dirty & diluted	U	10	10

[a] Shall be free of turbidity.

B.4.8 Target Values for Alpha Counting Measurements for Waste Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
Liquid Waste/HAW	Pu	10	10
/MAW	Pu	5	5
/LAW	Pu	5	5
U,Pu Solutions/Waste	U	5	5

B.4.9 Target Values for IDMS Measurements for Process, Product, and Waste Materials

Material/Type	Element	Precision % Rel. Ran. Error	Bias % Rel. Sys. Error
Spent Fuel inputs/	U	0.5	0.5
HWR & LWR	Pu	0.5	0.5
Spent Fuel Inputs/FBR	U	0.5	0.5
	Pu	0.5	0.5
U,Pu Solutions/Waste	U	0.5	0.5
	Pu	0.5	0.5

B.4.10 TARGET VALUES FOR UNCERTAINTY COMPONENTS IN ISOTOPIC ASSAY

Isotope	(%) Abund.	GMS[a] Prec.[h]	GMS[a] Bias[i]	TIMS[b] Prec.	TIMS[b] Bias	Gamma Spec.[c] Prec	Gamma Spec.[c] Bias	Alpha Spec. Prec	Alpha Spec. Bias	IDMS[d] Prec	IDMS[d] Bias
^{235}U	0.2[e]	0.1	0.1	0.7	0.5	5	3	--	--	0.5	0.5
	0.7[e]	0.05	0.1	0.5	0.5	2	1	--	--	0.5	0.5
	3[e]	0.03	0.1	0.3	0.3	0.5	0.5	--	--	0.5	0.5
	20[f]	0.02	0.1	0.1	0.1	0.5	0.5	--	--	0.5	0.5
	90[f]	0.01	0.03	0.05	0.05	0.2	0.5	--	--	0.5	0.5
^{238}Pu	0.3[g]	---	---	2	2	--	--	2	2	--	--
	1.5[g]	---	---	0.7	0.7	--	--	3	2	--	--
^{239}Pu	50-80[g]	---	---	0.1	0.1	--	--	--	--	0.3	0.3
^{240}Pu	10-30[g]	---	---	0.2	0.2	--	--	--	--	--	--
^{241}Pu	3[g]	---	---	0.3	0.3	--	--	--	--	0.3	0.3
	15[g]	---	---	0.3	0.3	--	--	--	--	0.3	0.3
^{242}Pu	1-5[g]	---	---	0.3	0.3	--	--	--	--	--	--

a Gas isotope mass spectrometry (UF_6).
b Thermal ionization mass spectrometry.
c Only for materials free of ^{232}U (^{232}U/^{235}U<10^{-9}).
d Isotope dilution mass spectrometry. Direct assay of isotope against spike, e.g. ^{233}U.
e All materials.
f Pure uranium compounds.
g Pure Pu materials.
h % Relative Random Error
i % Relative Systematic Error

Appendix B.5 TYPICAL AMOUNTS OF ELEMENT NEEDED TO PERFORM ONE MEASUREMENT

Method	U	Pu	Unit
Titrimetry	20-100	5-50	milligram
Coulometry	2-20	2-10	milligram
Gravimetry	2-20	0.2-3	gram
X-ray Fluorescence	0.1-30	0.1-30	milligram
IDMS[a]	10-1000	1-1000	microgram
Spectrophotometry	20-500	1-100[b] 0.1-10[c]	microgram milligram
Fluorimetry	2-500	---	nanogram
Alpha Counting	2-500	0.1-1	microgram
K-edge Densitometry	0.2-1	0.3-1	gram
Gas MS[a]	20	---	milligram
Thermal Ion. MS[a]	1-1000	1-1000	microgram
Gamma Spectrometry	0.1-1	---	microgram
Alpha Spectrometry	---	0.1-1	microgram

a Amount of sample required. In these cases an analysis can be performed on smaller amounts of element.
B Colorimetry
c Direct measurement at 830 nm of Pu (VI).

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APPENDIX C: **An Example of Using an MBA Inventory Difference Limit to Estimate Uncertainty Criteria for Destructive Assay Measurements**

Introduction. The question of how "good" do analytical chemistry measurement need to be to meet safeguards goals can be estimated by evaluating all measurements performed for a material balance area (MBA). To begin this process, one must first establish a goal-quantity for detection of theft. One criteria for making this goal-quantity is the IAEA "Significant Quantity" of 8 kg Pu and 25Kg ^{235}U. These significant quantities are probably for inventory differences (ID) of entire sites and too large for a single MBA in a facility. A more realistic goal-quantity is the US DOE criterion of 2% of the MBA throughput. The most restrictive criteria is that of the US NRC allowable IDs. They are typically <1% of throughput for U and <0.5% for Pu.

Estimation Procedure.   The steps one may follow to estimate the material measurement uncertainties required for theft detection are:
1. Determine the MBAs for the facility.
2. Establish the safeguards goal-quantity for the MBA and the statistical tests and degree of confidence to be associated with the detection of an inventory difference.
3. Determine the inventory period (monthly, bimonthly, etc.) for each MBA.
4. Determine the quantity and type of special nuclear material (SNM) stored in or processed in each MBA.
5. Establish key measurement points (KMP) for each MBA.
6. Identify the destructive analysis (DA) and non-destructive analysis (NDA) measurements to be used for SNM control (or process control or QA) for each MBA.
7. Make a chart or table showing the quantities of SNM, which will be measured at each KMP for each inventory period and the uncertainties, systematic and random, for each measurement method. These uncertainties may be estimated or, in the case of this example, the DA uncertainties left as unknowns to be determined. In addition to measurement errors, uncertainties should include all known sources of variation such as sampling errors, moisture uptake, and temperature and pressure effects.
8. Calculate the measurement uncertainties for each inventory period's SNM flow and beginning and ending inventories.
9. Combine these uncertainties and subtract the combined uncertainties from the total allowable uncertainty for theft detection. The difference will be the uncertainty "budgeted" for DA.
10. From this DA uncertainty 'budget', calculate the target uncertainty values for the DA methods.

This process is involved and material flows may not be well known at the beginning or NDA measurement uncertainties may not be well known. However, the factors that do not contribute much to the overall uncertainty can be roughly estimated. If 'conservative or somewhat overstated' estimates are made for the critical parameters, the final result will be a 'worst case' estimate. Often such an estimate is adequate for making DA upgrades decisions.

The outcome of such analyses will differ widely with the nature of the MBA and the confidence level desired for the detection of a diversion. For instance the acceptable random error for a measurement will be quite different depending on whether it is a single measurement of a large quantity of material or measurements on a large number of objects. For this appendix, a specific example has been selected and the parameters varied to show their relative effect. **The reader is reminded that the following discussion is only an example and should not be considered as typical or representative of a real situation. It is particularly important to note that the statistical treatment used has been simplified.**

Estimation Example. Consider the case of a MOX reactor fuel production facility that uses low burnup Pu and natural uranium oxides to make fuel pellets. A flow diagram for this facility is shown in Figure 1.
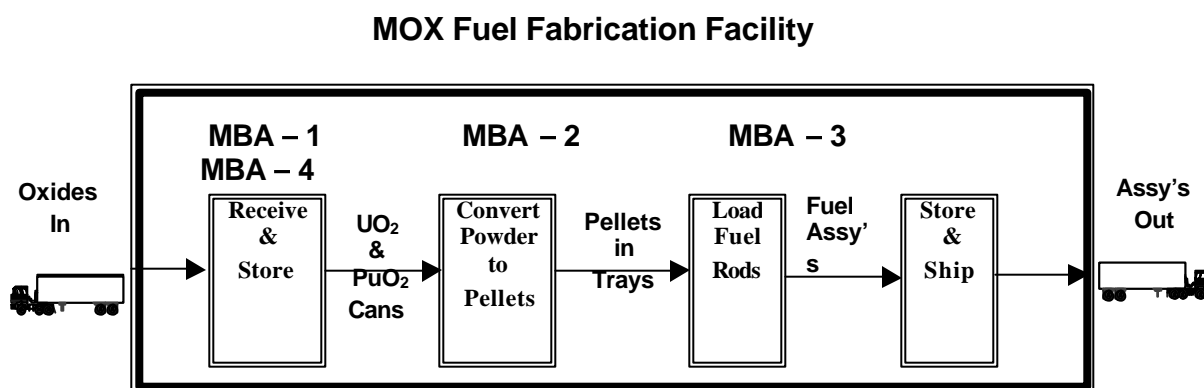
MOX Fuel Fabrication Facility

Figure 1

Step 1: Defining MBA's is outside the goal of this exercise. Take them as given in Figure 1.

Step 2: For this example only MBA-2, where oxide powder is converted to pellets, will be considered. The DOE 2%-of-throughput criterion will be used. Having identified the goal-quantity, one must decide on the statistical tests to be used to identify whether observed IDs are "real". In addition IDs that are less than the goal-quantity, would be used to identify significant problems with the system. Confidence levels for both "false positives" and "false negatives" should also be established. These issues are beyond the scope of this appendix. The reader should consult statistical texts such as references 3-6 for more details on this subject. For this exercise, the statistical significance of the uncertainties associated with measurements at the various parts of the process will not be specified. For a real situation, one must make a determination of the desired level of confidence required before identifying an inventory difference as such. To increase confidence that differences are "real", "wider" errors would be used. Unfortunately while decreasing the number of "false positives", this increases the chances of "false negatives"; *ie,* not detecting diversions. In order to detect a goal-quantity ID, the total error "budget" for measurements, including DA, must be less than the goal-quantity**. For this example, the error budget will be taken as one half to the goal-quantity** The relationships among bias, precision, and number of samples will be illustrated.

Step 3: Accountancy will be monthly.

Step 4: Because the facility uses natural uranium (not an SNM), uranium can be ignored. Only Pu needs to be considered. Assume the "beginning inventory" is the same as the ending inventory for the prior month and consists of one input can containing 2 kg of Pu as PuO_2 plus one tray of MOX pellets containing 1.9 kg Pu. All scrap is removed from the MBA before the ending inventory, i.e. the MBA is cleaned out between inventories. Assume holdup is measured annually, and does not contribute significantly to a single month ID. Finally assume the end of month inventory is the same

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[3] M. G. Natrella, Experimental Statistics: Handbook 91, U.S. Government Printing Office, Washington, 1963.

[5] Guide to the Expression of Uncertainty in Measurement, ISO/TAG4/WG3, June 1992.

[6] Evaluation and Control of Inventory Differences in the DOE Complex, TSO-87-9/BNL-40221, J. Sanborn, August 1987.

as the beginning inventory. During the month the material flowed as follows: "N" new cans of Pu oxide each containing 2 kg Pu entered the process and the oxide was converted into MOX pellets; N trays of MOX pellets, each containing 1.9 kg Pu, exited the process. The balance of the material (5% or 0.1 kg (Pu)/can) was in the form of scrap powder. Defining throughput as the sum of inputs and outputs from the MBA, the throughput was 2N kg of Pu. Based on the 2% of throughput criteria for a theft-detection goal-quantity, the MBA 2 goal-quantity is 2% of 2N kg Pu. The value of N will be allowed to vary to illustrate the effect of the number of items on permissible uncertainties.

Step 5: Within MBA-2 samples will be taken for assay of both incoming and outgoing material. Figure 2 illustrates this MBA's SNM flows and locations of KMPs with their associated measurement methods.
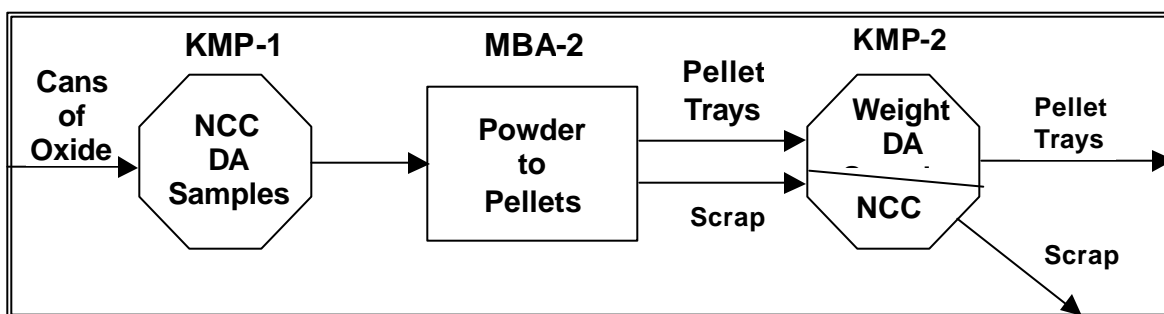

Figure 2. Key Measurement Points in MBA-2

Step 6: The measurements applied to the inventories and material flows are as follows:

The PuO$_2$ can "passport" (shipper) values are used until the cans arrive at KMP-1.

Upon receipt at KMP-1, incoming cans are measured by neutron coincidence counting (NCC) and gamma spectroscopy to confirm the passport values The cans are then weighed and sampled. The samples are submitted for Pu assay by DA techniques.

Before leaving the MBA through KMP-2, MOX pellets in trays are weighed and samples taken for DA. Confirmatory measurements by NCC and gamma spectroscopy may also be made.

Scrap; *i.e.,* oxide powder spilled or otherwise not successfully converted to pellets, is collected, weighed, and measured by NCC. This is also done at KMP-2.

Step 7: Table 1 summarizes the quantities of SNM, the measurement methods and systematic (bias) and measurement (random) uncertainties. . Because this exercise is to evaluate the permissible DA uncertainties, approximate weighing and NDA measurement uncertainties have been assigned without further justification. "TBD" means "To Be Determined." In this example, errors associated with sampling the powder and the pellets may be thought of as included in the errors of the measurement method. In a more realistic case, the sampling errors and statistical methods of sampling should be treated explicitly.

Table 1. Summary of Material Quantity, Measurements and Measurement Uncertainty Data

KMP #	Material Form and Pu mass, kg	Measurement Method	Bias (Systematic uncertainty, %)	Precision (Random uncertainty, %)
1	PuO$_2$ powder cans 2 kg/can	Weight	0.1%	0.2%
1	PuO$_2$ powder samples	DA	TBD	TBD
1	PuO$_2$ powder cans, 2 kg/can	NCC + gamma Spectroscopy	confirmatory	confirmatory
2	ScrapU/Pu oxide can 5% of total Pu	NCC	5%	2%
2	MOX Pellets in trays	NCC + gamma Spectroscopy	confirmatory	confirmatory
2	MOX Pellet Samples	DA	TBD	TBD
2	MOX Pellets in trays	Weight	0.5%	0.2%

Step 8: Calculate the uncertainties for the mass of Pu flowing through MBA-2 over the 1 month period and for the mass of Pu present in the beginning and ending inventory.

Tables 2 and 3 show the uncertainties, expressed as Pu mass, for the beginning and ending inventories and monthly throughput, respectively. The exact method for combining uncertainties can be complex. For a first approximation, one can add the systematic errors linearly and the random errors quadratically; *ie,* use the square root of the sum of the squares of the individual random uncertainties.

Table 2. Beginning and Ending Inventory Measurement Uncertainties

Pu Form and Mass	Measurement	Bias (Systematic uncertainty, kg)	Precision (Random uncertainty, kg)
1 Can of PuO$_2$ powder 2 kg Pu	Weighing	0.002	0.004
Samples from above can of powder	DA	TBD	TBD
1 tray of MOX pellets 1.9 kg Pu	Weighing	0.010	0.004
Samples from above MOX pellet tray	DA	TBD	TBD

Table 3. Monthly Throughput Measurement Uncertainties

Pu Form and Mass	Measurement	Bias (Systematic uncertainty, kg)	Precision (Random uncertainty, kg)
N cans PuO_2 powder 2 kg Pu each	Weighing	N x 2 x 0.001	Sqrt(N x (2 x 0.002)^2)
Samples from above cans of powder	DA	TBD	TBD
15 trays MOX pellets 1.9 kg each	Weighing	N x 1.9 x 0.005	Sqrt(N x (1.9 x 0.002)^2)
Samples from above trays of pellets	DA	TBD	TBD
Scrap U/Pu powder 5% of total Pu (1 can)	NCC	N x 2 x 0.05 x 0.05	N x 2 x 0.05 x 0.02

Step 9: Combine the uncertainties for the monthly throughput, and the beginning and ending inventories adding the systematic uncertainties directly and the random uncertainties quadratically. To satisfy the aim of being able to detect the theft of a "goal-quantity" of material, the overall uncertainty must be less than the goal-quantity. A conservative method for combining the systematic and random errors to obtain the overall uncertainty on the inventory is to add them together linearly. In this example, the resulting equation for the overall uncertainty has 5 unknowns – number of cans, bias and precision of both the DA of the powder and the DA of the pellets. To simplify we will combine the DA uncertainties of the powder and pellets and consider only the total DA precision and accuracy budget.

Step 10: One must now determine the target uncertainties for the DA method(s). Given that the equation for the overall uncertainty has three unknowns, it has a family of solutions. An easy way to study the effects of the various variables is to use a spreadsheet to model the behavior. If one fixes the number of cans and assumes the DA uncertainty is dominated by bias, one can set the precision uncertainty to zero and iteratively enter bias values until the calculated uncertainty equals the target value. One can then assume the DA uncertainty is dominated by precision and repeat the exercise. This sets the limits for the set of solutions. Intermediate cases can then be calculated. Finally, the number of cans can be changed and the calculations repeated. Results for several cases are presented in Figure 3. For a given number of cans, all points lying to the left of the line are combinations of bias and precision that will allow the DA goal to be met.

From Figure 3 one sees that both the precision and bias requirements for the DA analysis become less severe as the number of items (cans in this example) increases. The effect is greater for precision because the chance of the mean being offset by poor precision decreases as the number of measurements increases. (Another advantage of sampling and measuring more frequently is that it reduces the chance of theft from any single item going undetected.) The allowable bias is substantially less than the allowable precision uncertainty. Even for 50 cans the maximum allowable bias is only 0.5%. If the bias is greater than this, it will be impossible to detect the diversion of a goal-quantity. This emphasizes the importance of recognized standards in determining bias.

If facilities employ gravimetric methods to assay their Pu and U oxides and metals. These methods, without impurity corrections, will be biased. If impurity corrections are made, the bias may be small. However, without standards bias estimates are subjective.

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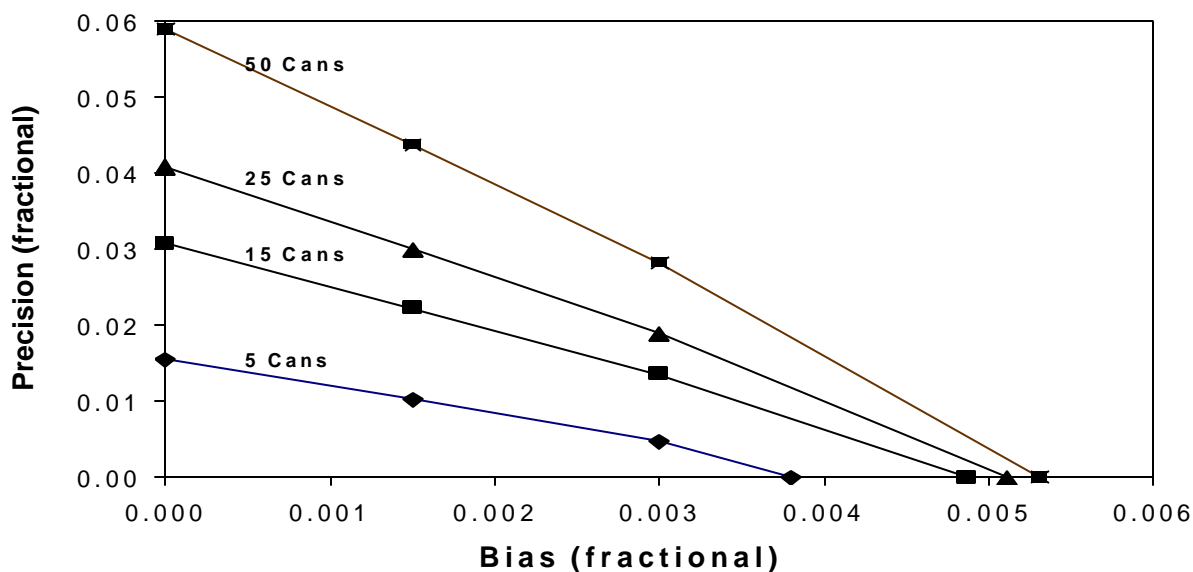

Figure 3

The fact that the allowed precisions shown in Figure 3 are as high as 6% results from the particular example used. It was not selected to represent a challenging situation and should not be interpreted as implying that precision is generally of little concern. It does illustrate the importance of evaluating the specific situation before committing to upgrades. Evaluations of the need for measurement upgrades, DA or otherwise, should include similar calculations for the MBAs evaluated.

Conclusion: Systematic evaluation of the bias and precision at each measurement point, allows the determination of how "good" a particular measurement needs to be and whether theft-detection at the goal-quantity level can be achieved. Even using estimates of some of the uncertainties, a systematic approach is useful in determining which errors are dominant, how to "budget" the allowable errors, and how to invest wisely to improve accountancy. The 10 step process described and the suggested simplifications and approximations facilitate a simple calculation to make assessments of the adequacy of existing methods or to determine what upgrades would be required to allow the DA method to meet theft detection goal quantities. While the example given is hypothetical, it illustrates how one must carefully identify and estimate systematic uncertainties, which may sum to become the dominant source of the overall uncertainty.

Destructive Assay Methods Compendium

Appendix D. References

1. <u>Handbook of Nuclear Safeguards Measurement Methods</u>, U.S. DOE Nuclear Regulatory Commission (NRC) Report, NUREG/CR-2078 (MLM-2855), D. R. Rogers, ed., Mound Laboratory, September 1983.

2. Annual Book of ASTM Standards, Volume 12.01 Nuclear Energy.

3. International Organization for Standardization, ISO Volume 27.120.30 Fissile Materials.